


Article

Concentration of Rare Earth Elements (Sc, Y, La, Ce, Nd, Sm) in Bauxite Residue (Red Mud) Obtained by Water and Alkali Leaching of Bauxite Sintering Dust

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Abstract: One of the potential sources of rare-earth elements (REE) is the industrial waste known as red mud (bauxite residue), in which the majority of REE from the initial bauxite are concentrated via the Bayer process. Therefore, the studies of the subject, both in Russia and outside, focus almost exclusively on red mud processing. This article looks into the possibility of REE concentration into red mud by leaching an intermediate product of the bauxite sintering process at Russian alumina refineries, namely electrostatic precipitator (ESP) dust. The experimental works were performed by X-ray diffraction (XRD) and electron probe microanalysis (EPMA) of the sinter and sinter dust. The determination of major and rare-earth elements in the sinter from the rotary kilns and in the ESP dust before and after leaching was carried out by X-ray fluorescence (XRF) and plasma mass spectrometry (ICP-MS). The study showed that it is possible to obtain red mud that contains three times more REE than traditional waste red mud after two-stage leaching ESP dust in the water at 95 °C followed by leaching in an alkaline-aluminate liquor at 240 °C. The shrinking core model was used to study the kinetics of leaching of the original ESP dust and water-treated dust in alkaline-aluminate liquor. The study showed the change in the limiting stage of the alkaline leaching process after water treatment, with the activation energy growing from 24.98 to 33.19 kJ/mol.

Keywords: rare-earth elements; scandium; alumina production; sinter processes; red mud; electrostatic precipitation dust; alkali leaching; kinetics

1. Introduction

The volumes of production/consumption of rare and rare-earth metals, which are critical for modern industries, are steadily increasing [1–4]. In this group of metals—scandium, yttrium, lanthanum, and lanthanides—scandium is the most scarce and commercially attractive one. The increased interest in scandium is associated with its application in various industries [5–7]. Small amounts of scandium are found in ores of aluminum, cobalt, iron, molybdenum, nickel, phosphate, titanium, tungsten, uranium, and others [8–16].

At the moment, phosphogypsum—waste from the processing of apatite concentrates [17,18]—and red mud (bauxite residue) are considered to be the most promising sources of scandium [19–24]. Phosphogypsum is also considered to be the most promising source of other rare earth metals [6],

as it may contain up to 1% of rare earth elements in total [25]. More than 250 million tons of phosphogypsum has been accumulated in Russia [26] with an annual increase by over 14 million tons. However, despite the large number of works devoted to the processing of phosphogypsum, there is still no commercially viable technology for its processing [27], which is explained by isomorphic co-crystallization of REE with gypsum, and therefore the need for its complete release [28].

Bauxite residue generated in the recovery and processing of bauxites is a source of environmental pollution [29,30] on the one hand and a promising object for obtaining valuable elements [31] on the other hand. Bauxite residue contains a high amount of scandium (70–260 ppm) that is close to its primary resources [32]. Large amounts of this waste form what may be called man-made deposits, which can be recycled into building materials, pigments, coagulants for wastewater treatment, and which can be used to re-extract alumina, extract iron concentrates, titanium, rare and rare earth metals [33–35]. In the industrial production of alumina, almost all Sc is concentrated in red mud. According to available estimates, the global reserves of scandium in the industrial waste range from 1 to 3 million tons, with 70–80% of it being contained in bauxite processing waste [36]. The full processing of the bauxite residue currently generated makes it possible to extract 6600–20,400 t of scandium per year. Therefore, a large number of studies have been dedicated to the recovery of rare-earth metals from various types of bauxite residue [37] obtained by processing various bauxites in the Bayer method and its variations. However, the low content of scandium in the red mud, the high content of alkali and alkaline earth metals, and the simultaneous recovery of iron together with REE [38] or low extraction efficiency [39,40] render the existing methods for extracting scandium from this type of industrial waste non-viable.

It should be noted that most studies of the separation of REE from alumina products have focused on the processing of red mud. In this article, we made an attempt to study the possibility of obtaining the REE concentrate from electrostatic precipitator (ESP) dust, which is an intermediate product of kiln sintering in alumina production. The dust is generated in a rotary kiln (Figure 1), where low-quality bauxite (the mass ratio of Al_2O_3 to SiO_2 (silicon modulus) is less than 7) is sintered with soda ash in order to convert the alumina-containing mineral into a water-soluble sodium aluminate. Iron and silicon-containing minerals react similarly with soda to form ferrite and sodium silicate, respectively. The technological process, especially at the drying and decarbonization stages, generates a large number of fine particles less than $100\text{ }\mu\text{m}$ (25–40% of the charge), which are carried away with the exhaust gases. To clean the exhaust gases of kilns from dust particles, a three-stage capture system is used. The first stage is the dust chamber where most coarse dust particles precipitate; the second stage is cyclones, where medium dust particles are removed from the exhaust gases through vortex separation; and the final stage is electrostatic precipitator. The last stage captures the finest particle fraction (less than $20\text{ }\mu\text{m}$) using the force of an induced electrostatic charge.

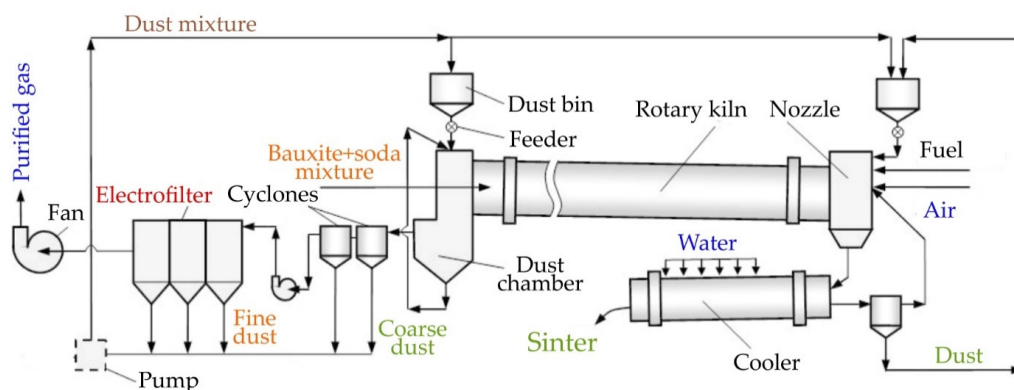


Figure 1. Flow chart of the sintering process on the RUSAL-Kamensk-Uralsky alumina refinery.

It is impossible to remove all dust from the technological process since that would upset the heat balance of the furnace and would greatly complicate the movement of the charge in the drying zone. On the other hand, the ESP dust acts mostly as a dead weight, since a number of dust circulations through the kiln are larger than through all other units of the gas treatment system. Electrostatic precipitators capture only the smallest particles, which often pass very quickly through the hot zones of the furnace, and the sintering process fails to complete. Ultimately, they acquire the charge of the electrostatic precipitator and are released into the atmosphere. The physicochemical properties of sintering dust and the possibility of their leaching together with bauxite had already been investigated in our previous work [41]. It was shown that ESP dust can be highly reactive and can be removed from the process with further leaching to extract useful components. Also, the high recovery rate of ESP dust means significant losses of secondary heat. The proportion of ESP dust in the total mass of dust is up to 15%, which means that alumina refineries in Russia produce more than 30 thousand tons of ESP dust per year. At the same time, ESP dust contains about 50 ppm of scandium [42]. Therefore, more than 1.5 t of scandium and even more of other rare earth metals can be obtained annually from this intermediate product.

In this work we studied the possibility of leaching ESP dust with water and mother liquor of the Bayer process in order to extract rare-earth elements into valuable components such as alumina, caustic alkali, and soda, and, at the same time, concentrate them in the red mud resulting from leaching.

2. Materials and Methods

2.1. Solid Phase Characterization

The phase and quantitative composition of the ESP dust from sintering kilns of the Kamensk-Uralsky alumina refinery and leaching products were determined by X-ray diffraction (XRD) on a Rigaku D/MAX-2200 diffractometer (Rikagu Corp., Tokyo, Japan) using the PDF-2 database (International Center for Diffraction Data) and by X-ray fluorescence (XRF) using an Axios MAX X-ray fluorescence spectrometer (Malvern Panalytical Ltd., Almelo, The Netherlands). The content of REE micro impurities in the feedstock and leachate was determined using inductively coupled plasma mass spectrometry (ICP-MS) on a PerkinElmer NexION 300S instrument (PerkinElmer Inc., Waltham, MA, USA).

Electron probe micro-analysis (EPMA) was performed using a Cameca SX 100 microanalyzer (CAMECA Instruments, Inc., Madison, WI, USA) equipped with an energy-dispersive X-ray spectroscopy analysis (EDS) module Bruker XFlash 6 (Bruker Nano GmbH, Berlin, Germany).

2.2. Reagents

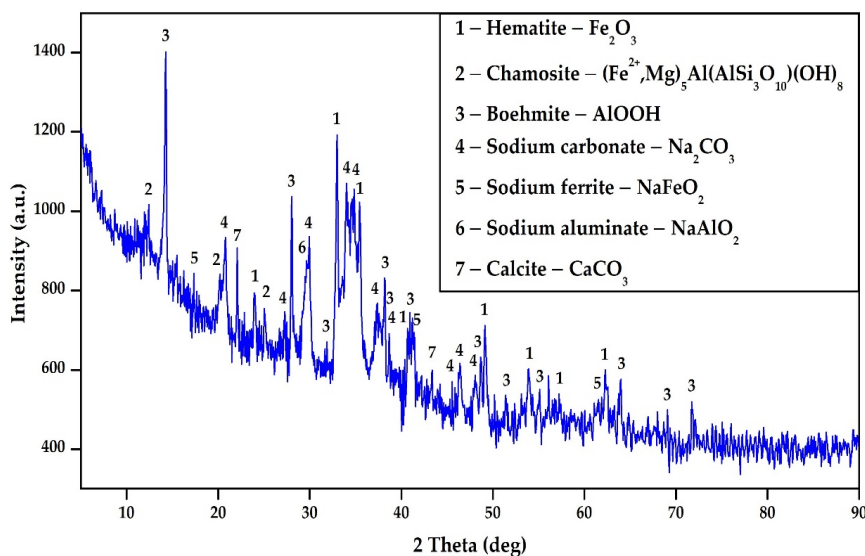
All reagents used in this study were of analytical purity. Distilled water was obtained using a GFL distiller (GFL mbH, Burgwedel, Germany). A model alkali liquor obtained was obtained by dissolving NaOH in distilled water. Then, the necessary amount of $\text{Al}(\text{OH})_3$ was dissolved in the resulting hot caustic alkali liquor to achieve the desired ratio of NaOH and Al_2O_3 in the model liquor. After complete dissolution of aluminum hydroxide, the liquor was brought to the required concentration in caustic alkali. The aluminate liquor had the following chemical composition: Na_2O_k (caustic alkali) = 240 g/dm^3 , Al_2O_3 = 120 g/dm^3 . The sinter and ESP dust were obtained from the RUSAL-Kamensk-Uralsky alumina refinery (56.304530, 61.980334; Kamensk-Uralsky, Russia) where low-grade bauxite is processed via combined Bayer-Sintering process. Bauxite with the high silica content is sent in rotary kiln together with sodium carbonate to obtain water-soluble sinter at 1150°C . The chemical and phase composition of the ESP dust and the sinter are different, since dust passes through the hot zone of the sintering kiln faster and many processes fail to complete; also, the difference may be caused by the difference in the distribution of minerals into different fractional classes. Table 1 shows the chemical composition of the ESP dust of the Kamensk-Uralsky alumina refinery, against the chemical composition of the bauxite sinter.

Table 1. The chemical composition of electrostatic precipitator (ESP) dust and bauxite sinter, wt. %.

Products	Al ₂ O ₃	SiO ₂	Na ₂ O	MgO	CaO	Fe ₂ O ₃	LOI ¹	μ _{Si} ²	ΣREE
ESP dust	25.5	2.5	28.3	0.4	2.5	12.2	24.8	10.2	755
Bauxite sinter	35.0	5.0	33.2	0.8	4.8	16.7	0.5	7.0	567

¹ LOI—loss on ignition at 1000 °C. ² μ_{Si} (silicon modulus)—mass ratio of Al₂O₃ to SiO₂.

The results of X-ray diffraction analysis of the electrostatic precipitator dust of the RUSAL-Kamensk-Uralsky alumina refinery is shown in Figure 2.

**Figure 2.** X-ray diffraction analysis of the electrostatic precipitator dust of the RUSAL-Kamensk-Uralsky alumina refinery in Russia.

2.3. Experimentation

The leaching of the required weight of ESP dust in distilled water was carried out at L:S = 10:1 at 95 °C for 60 min in a 0.5 dm³ Lenz Minni thermostatic reactor (Lenz Laborglas GmbH & Co. KG, Wertheim, Germany) fitted with an overhead stirrer and ports for a refrigerator and samplers.

Autoclave leaching of the ESP dust sample at L:S = 3:1 was carried out at 160, 200, and 240 °C in an aluminate mother liquor for 15–90 min in a 1 dm³ Parr autoclave (Parr Instrument, Moline, IL, USA). Leaching in an aluminate liquor at 90 °C also used a thermostatic Lenz Minni reactor.

After water and alkaline leaching, the resulting red mud was separated from the aluminate liquor by filtration on a Buchner funnel. After washing and drying of the bauxite residue for 8 h at 110 °C, the content of rare-earth elements and other components was measured. The solid phase obtained after water leaching of ESP dust is designated as ESPDW, and that obtained by autoclave leaching with an alkaline aluminate liquor at 240 °C for 90 min is designated as ESPDA.

3. Results and Discussion

It can be seen from Table 1 that the chemical composition of ESP dust and bauxite sinter are different. The high LOI in the dust is associated with the incomplete decomposition of soda and calcite; however, there is also a significant decrease in the content of silica, magnesium, and calcium in dust relative to alumina and an increase in sodium content. A decrease in silica content in dust leads to a significant increase in the silicon modulus (μ_{Si}). The results of X-ray diffraction analysis (Figure 2) confirm the presence of sodium aluminate in the ESP dust; however, most of the soda remains unreacted.

According to the previous research [19,21,43,44], the REE and Sc are possibly adsorbed on goethite, hematite and in the channels of aluminosilicates in the typical Bayer bauxite residue. The primary container of these elements could be cancrinite [45]. However, during the sintering process iron minerals are transformed into sodium ferrite and aluminosilicate—into sodium silicate and sodium aluminate (Figure 2). Therefore, REE and Sc could be liberated through the sintering process, which could lead to an increase in their concentration in the by-products and increased leachability than in typical Bayer bauxite residue.

Figure 3 shows the content of rare-earth elements in ESP dust and sinter. The obtained data show that the ESP dust from the sintering process contains more REE than the sinter itself. Moreover, if we detract LOI (consisting of water and CO₂ carbonates, which are removed from sinter at 1000 °C and which remain in ESP dust, according to Table 1), the REE content in the calcined ESP dust will be approximately 70–80% higher than in the sinter. The obtained data is in good agreement with the results presented previously in the patent [42], where it was shown that ESP dust contains about 50 ppm of scandium. This may be due to the repeated circulation of fine dust in the process and mineralogical transformation. Consequently, ESP dust can be a source of REE, and we can consider the option of removing it from the cycle in order to extract valuable components and increase the efficiency of the sintering kiln.

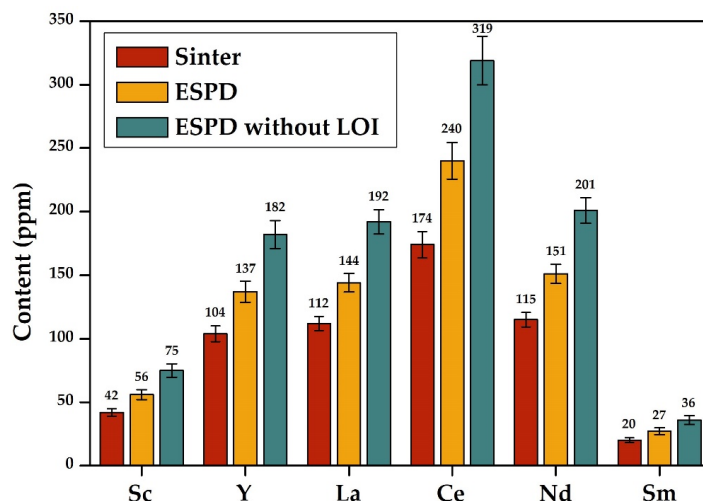


Figure 3. Content of rare earth elements in electrostatic precipitator dust and bauxite sinter, ppm (LOI—loss on ignition at 1000 °C).

3.1. Water Leaching of ESP Dust

The XRD analysis of ESP dust (Figure 2) shows a high content of soluble minerals (such as sodium silicate and sodium aluminate). Tests were carried out to leach ESP dust with water for 1 h at 95 °C, which is necessary for the complete conversion of sodium salts into liquor. The output of the solid phase (ESPDW) after leaching was 40% of the initial weight of ESP dust. Table 2 shows the chemical composition of the resulting red mud, and the degree of recovery of the main components into the liquor is shown in Figure 4. Part of the aluminum in electrostatic precipitator dust was converted to sodium aluminate; it is therefore easily leached with water. Notably, aqueous leachate has a higher silicon modulus than the original dust, as silicon has a degree of recovery higher than aluminum. This indicates that the degree of transformation of silica to sodium silicate is higher than alumina to sodium aluminate. Na₂O is almost completely leached, which indicates that with water leaching for less than 1 h the components in the resulting liquor do not have time to form a disilication product according to the following Equation (1):



where X represents various inorganic anions, most often sulfate, carbonate, chloride, aluminate, etc. [46].

Table 2. The chemical composition of electrostatic precipitator dust after water leaching, wt. %.

Product	Al ₂ O ₃	SiO ₂	Na ₂ O	MgO	CaO	Fe ₂ O ₃	LOI	μSi
ESPDW	39.8	3.1	1.7	1.0	6.2	30.5	18.3	12.8

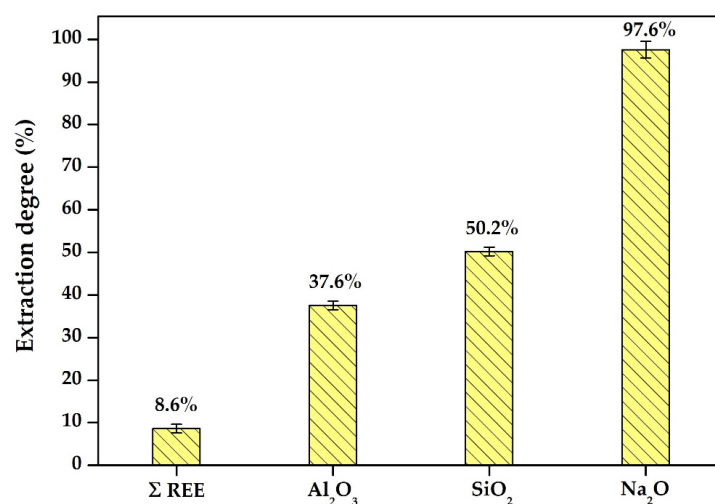


Figure 4. The extraction degree of the main components into the liquor by water leaching of electrostatic precipitator dust.

It can also be seen in Figure 4 that REE (Sc, Y, La, Ce, Nd) are slightly extracted during water leaching, because of their interaction with alkali and soda [47]. As shown in some studies [39,40], the degree of scandium recovery from red mud to soda liquor usually does not exceed 20%.

As it was stated in the introduction section, scandium is the most valuable REE in red mud. It was previously shown that scandium in red mud is mainly associated with iron minerals [48]. However, some researches show [45] that cancrinite could accumulate Sc as well. Therefore, to study the association of rare-earth metals with different phases, we performed ESPD and ESPDW surface mapping using EPMA (Figure 5).

It can be seen from Figure 5 that scandium in ESP dust is mainly associated with iron minerals, and to a lesser extent—with silicon compounds. It could be associated with the fact that iron minerals (hematite) are not fully transformed into sodium ferrite during sintering because small particles of dust pass very quickly through the hot zones of the furnace and a disilication product is not formed yet. Almost the same picture is observed in ESPDW; however, the distribution of scandium is more uniform than in ESP dust. This may be due to the formation of a disilication product (sodalite or cancrinite), which can adsorb the REE. This suggests that destruction of the hematite matrix is required at first for the complete recovery of REE from ESPD, as is the case with the typical Bayer process red mud. This also explains the low degree of REE recovery at the water leaching stage, since hematite cannot be dissolved by sodium carbonate liquor.

3.2. Kinetics of ESP Dust Leaching by Alkaline Aluminate Liquor

To study the mechanism and effect of temperature on the leaching of initial ESPD and ESPDW with the alkaline aluminate mother liquor, experiments were carried out to measure the aluminum extraction degree from the liquor with variable duration and temperature of the process. Aluminum was chosen as an indicator of leaching efficiency as it was the only element extracted from the liquor during alkali leaching of ESPDW. The temperature range was selected, taking into account that,

after the extraction of readily soluble sodium salts, the alumina in the material is mainly represented by boehmite, the leaching of which requires a temperature of more than 160 °C [49]. The experimental results are shown in Figure 6.

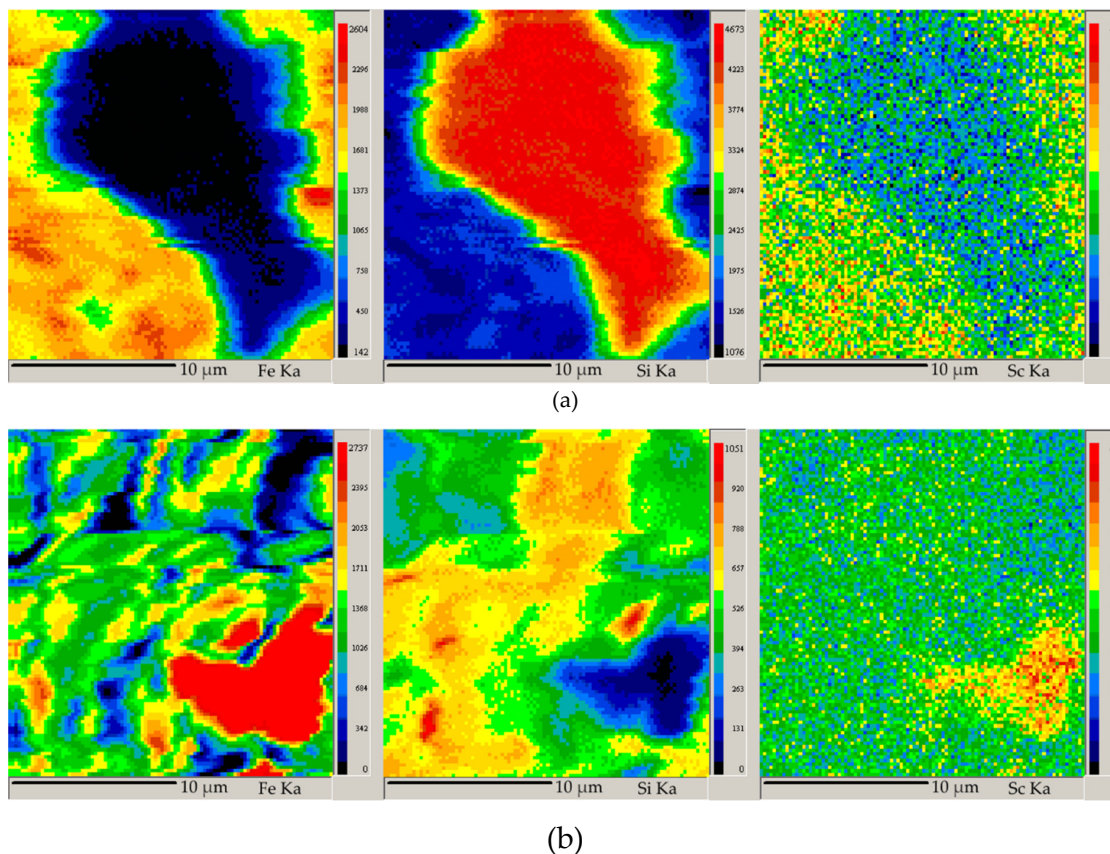


Figure 5. Mapping of electrostatic precipitator dust surface (a) and water-leached electrostatic precipitator dust surface (b) using the electron probe micro-analyzer.

It can be seen from Figure 6 that the kinetics of aluminum extraction into the liquor is quite high at all temperatures for the first 30 min for ESP dust. Even at 90 °C, more than 40% of aluminum is extracted from ESP dust after 30 min, apparently because of a certain degree of conversion of boehmite to sodium aluminate in the sintering kiln. However, after pre-leaching in water (ESPDW), sodium aluminate had already been extracted into the first-stage liquor; therefore, the rate of leaching of aluminum from ESPDW at 90 °C is significantly lower. Although at higher temperatures, due to a lower silica content, the efficiency of alumina recovery from ESPDW increases, reaching 90% after 90 min of leaching at 240 °C.

To study the leaching mechanism, the obtained kinetic curves were processed using the shrinking core model [50]. We studied six kinetic equations [51] describing the process in various modes, from kinetic to intra-diffusion; however, the models shown below (Equations (2) and (3)) proved to be most promising for the process description:

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = k_1 t, \quad (2)$$

$$1/3 \ln(1 - X) + ((1 - X)^{-1/3} - 1) = k_2 t, \quad (3)$$

where X is the degree of aluminum recovery into the liquor at a time t , k_i is the apparent rate constant. Equation (2) describes the process in the intra-diffusion area, while Equation (3) describes the process limited by interfacial transfer and diffusion through the product layer. The plot of $1/3 \ln(1 - X) +$

$((1 - X)^{-1/3} - 1)$ versus t for ESP dust leaching gives a straight line (Figure 7a) with the determination coefficient R^2 the highest among all models used (more than 0.98 for all temperatures except 90 °C), which indicates that leaching, in this case, is most likely limited by interfacial transfer and diffusion through the product layer. It can be concluded that during leaching, a disilication product is formed around the core of the boehmite (Figure 8), which slows down the leaching process. Also, a film of sodium titanate can form on the surface of boehmite, which is known [52] to reduce the rate of dissolution of aluminum hydroxides significantly. For water-leached dust, the highest determination coefficient is observed, when using Equation (2) (Figure 7c), which implies that the process is limited by diffusion through the layer of the product or unreacted matter.

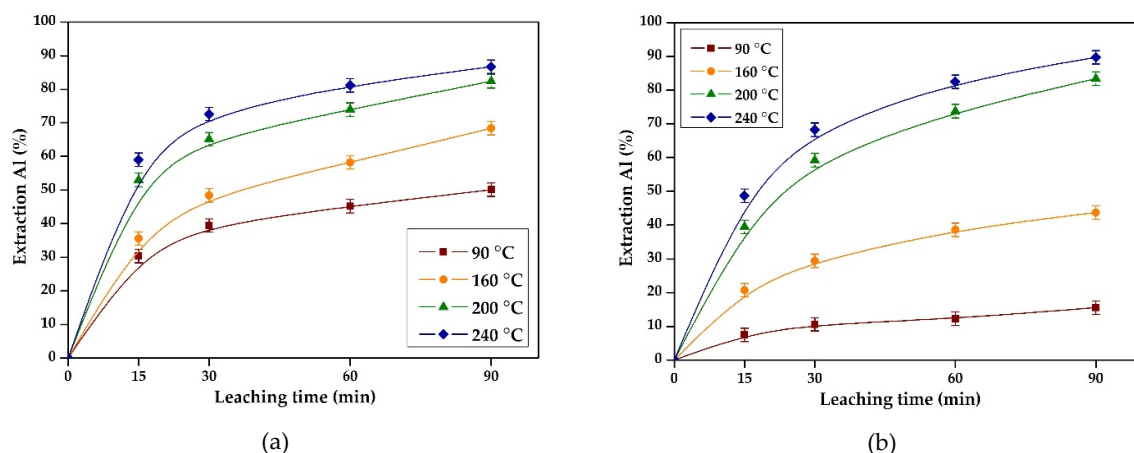


Figure 6. Effect of leaching time and temperature for Al extraction from raw ESP dust (a), from water-leached ESP dust (b).

Using the obtained values of the apparent rate constant (k_i) in Figure 7b,d and the Arrhenius equation (Equation (4)), we determined the values of the apparent activation energy for leaching ESPD and ESPDW (Figure 6) to be 24.98 kJ/mol and 33.19 kJ/mol, respectively.

$$k_i = A \exp(-E_a/RT), \quad (4)$$

where A is the Arrhenius constant, R is the universal rate constant (8.314 J/mol·K), T is the temperature (K), E_a is the apparent activation energy (J/mol).

The obtained values of the activation energy also confirm diffusion limitation. However, for an intradiffusion stage, the activation energy should be in the range of 8–22 kJ/mol. The higher values, in this case, maybe due to the fact that higher activation energy is required for the dissolution of the boehmite since a temperature of more than 160 °C is required for its extraction into alkali liquor. In the second case, the activation energy is higher, since there is no easily soluble phase of aluminum left after water leaching and a low degree of leaching efficiency of boehmite is observed at 90 °C.

Figure 8 shows XRD patterns of ESPDW and ESPDA, from which it can be seen that alkaline leaching results in disappearing of boehmite peaks and appearing instead of the peaks corresponding to cancrinite; iron, in contrast to the Bayer red mud, is represented by both hematite and hydroxide phases.

The yield of solid residue (red mud) from the leaching of ESPD in alkaline aluminate liquor at 240 °C for 90 min was 29.8% of the initial weight of dust. At the same time, the yield of red mud (ESPD), after ESPDW leaching with alkali liquor at 240 °C for 90 min was 21.0%. As a result, the degree of REE enrichment of red mud in the second case was higher. Figure 9 shows the content of rare earth metals in these products.

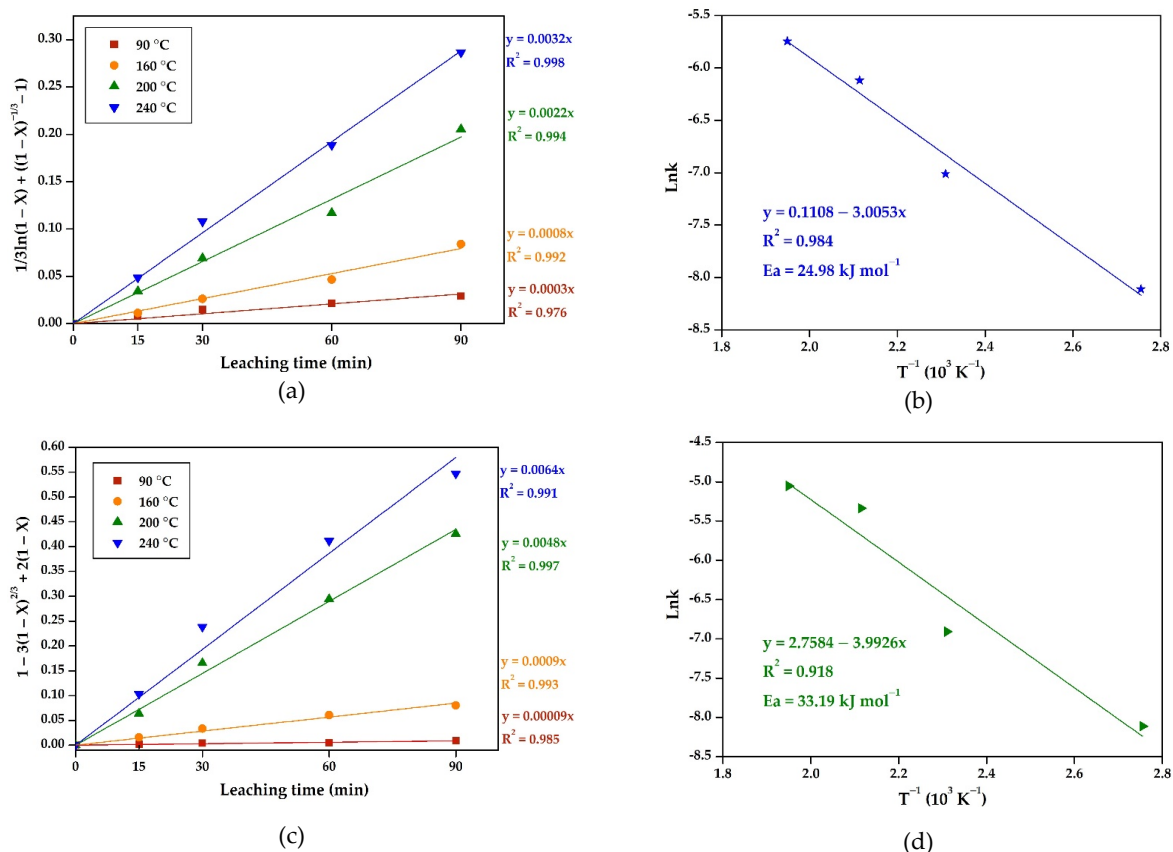


Figure 7. Results of substituting the data for ESPD leaching to Equation (3) (a); substituting the data for ESPDW leaching to Equation (2) (c); dependence $\ln k - T^{-1}$ for leaching the original ESP dust (b) and water-treated ESP dust (d).

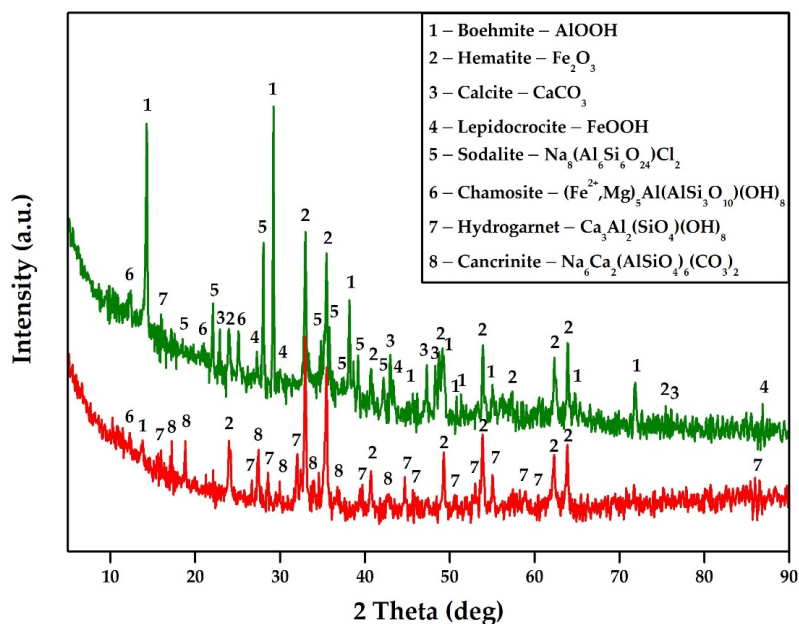


Figure 8. XRD pattern of water-leached electrostatic precipitator dust (green) and alkali-leached electrostatic precipitator dust (red).

The data in Figure 9 show that the total amount of REE in the red mud after ESP dust leaching was more than 1700 ppm in the first process and over 3200 ppm in the second process. Thus, we demonstrated

that, in principle, it is possible to concentrate rare-earth elements in red mud by leaching ESP dust with water and alkaline aluminate liquor. The REE content in the red mud obtained thereby is three times higher than in conventional red mud of the alumina refinery, which can significantly reduce the cost of obtaining the REE concentrate in the future. Moreover, the recovery of additional components from natural raw materials can improve the efficiency of processing of bauxite raw materials in general. Based on these findings, we propose the following ESPD processing scheme (Figure 10), which enables efficient recovery of both alumina and rare earth elements. The stage of leaching REE from ESPDA will be discussed in the next paper.

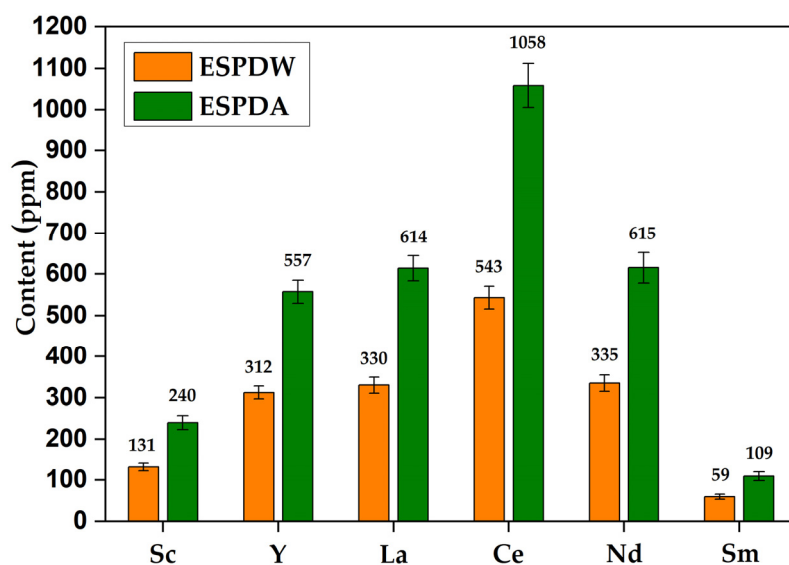


Figure 9. Content of rare earth elements in water-leached electrostatic precipitator dust and alkali-leached electrostatic precipitator dust.

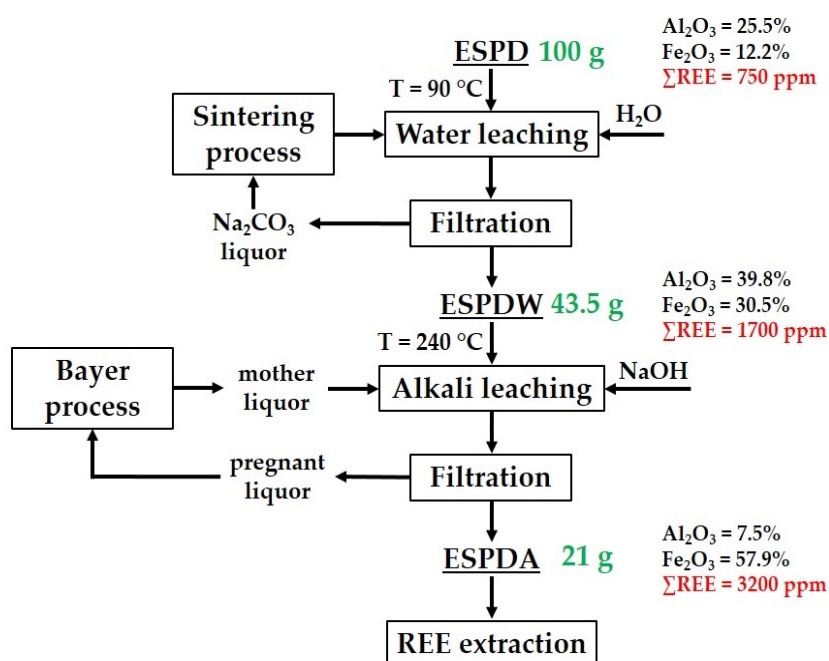


Figure 10. A flowsheet of rare-earth elements (REE) concentration from electrostatic precipitator dust by water/alkali leaching.

4. Conclusions

In this article, we investigated the possibility of concentrating rare-earth elements into red mud obtained by leaching dust from electrostatic precipitators used in bauxite charge sintering. We compared the chemical composition of the sinters and ESP dust formed during bauxite sintering in tubular rotary kilns. The sinter and the dust were analyzed for the content of rare earth elements. We also studied their association with various minerals of the materials used. The study of leaching of electric precipitation dust allows us to draw the following conclusions:

1. The chemical and phase composition of the electrostatic precipitation dust and sinter obtained in the same technological process are different. The content of rare-earth elements in the dust of electrostatic precipitators is 70–80% higher than in the sinter, which may be explained by a large number of cycles of ESP dust return to the kiln due to the very small size of particles.
2. Similar to the red mud of the Bayer process, scandium in ESP dust and in the solid residue after ESP dust leaching is associated to a greater extent with hematite, because of an insufficient transformation of latter into sodium ferrite in the sintering process and to a lower extent with disilication product (sodalite and cancrinite); the complete recovery of REE requires the destruction of the hematite at first.
3. The following conditions allow to obtain red mud from ESP dust that contains three times more REE than traditional waste red mud of the Ural Alumina Refinery: pre-leaching with water at 90 °C followed by autoclave leaching with an alkaline-aluminate liquor at 240 °C for 90 min.
4. The kinetic patterns of leaching alumina with the alkali liquor have been studied for the original electrostatic precipitation dust and water-leached dust. The change in the limiting stage of the process after water-treatment has been shown by an increase of the activation energy from 24.98 to 33.19 kJ/mol; changes in the form of the kinetic curves have also been demonstrated.

A technological scheme has been proposed for the removal of ESP dust from the cycle and its further comprehensive processing. Recovery of additional components from ESP dust will improve the efficiency of processing of bauxite raw materials in general and reduce the environmental footprint.

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Conflicts of Interest: The authors declare no conflict of interest.

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